

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 January 2007 (18.01.2007)

PCT

(10) International Publication Number
WO 2007/007107 A1

(51) International Patent Classification:

B01J 23/50 (2006.01) **B01D 53/94** (2006.01)
F02D 41/02 (2006.01) **F01N 3/08** (2006.01)

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(21) International Application Number:

PCT/GB2006/002595

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(22) International Filing Date: 12 July 2006 (12.07.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0514188.2 12 July 2005 (12.07.2005) GB

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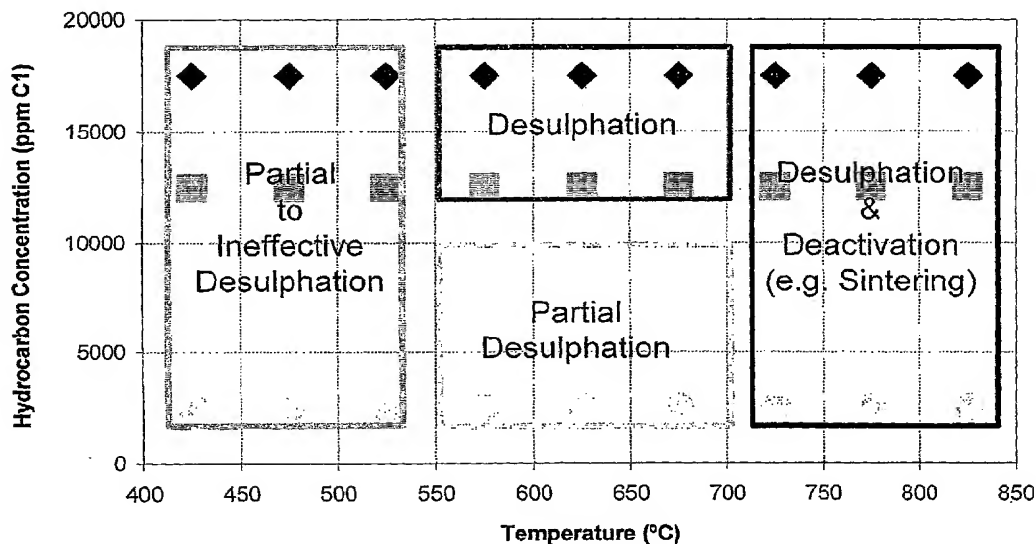
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AF, AG, AI, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GIL, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: DESULPHATING Ag/Al₂O₃ HC-SCR CATALYST



(57) Abstract: A method of desulphating a Ag/Al₂O₃ hydrocarbon selective catalyst reduction (HC-SCR) catalyst in an exhaust system of a lean burn engine, the method comprising contacting the catalyst with a lean exhaust gas stream comprising an elevated quantity of hydrocarbon species relative to normal engine operation at a temperature of from 550 to 700 °C, wherein the hydrocarbon species comprises cracked engine fuel. An exhaust system suited for use in the above method, and a lean burn engine and vehicle incorporating such an exhaust system, are also disclosed.

WO 2007/007107 A1



Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESULPHATING Ag/Al₂O₃ HC-SCR CATALYST

This invention relates to a method of desulphating a Ag/Al₂O₃ hydrocarbon
5 selective catalytic reduction (HC-SCR) catalyst in a lean burn engine exhaust gas
stream.

HC-SCRs are sometimes also referred to in the literature as non-selective
catalytic reduction (NSCR) catalysts, lean NO_x catalysts (LNC), lean NO_x reduction
10 catalysts, "DeNO_x catalysts" and NO_x occluding catalysts.

In hydrocarbon selective catalytic reduction hydrocarbons (HC) react with
nitrogen oxides (NO_x), rather than oxygen (O₂), to form nitrogen (N₂), carbon dioxide
(CO₂) and water (H₂O) according to Reaction (1):

15



The competitive, non-selective reaction with oxygen is given by Reaction (2):

20



HC-SCR catalysts used to selectively promote the desired reaction (1) include
Pt/Al₂O₃, Cu exchanged ZSM-5 and Ag/Al₂O₃. Ag/Al₂O₃ catalysts operate at higher
temperatures and over a broad temperature range, and have recently shown promise in
25 vehicle testing (Klingstedt et al., Topics in Catalysis, 30/31, 2004, 27 and Lindfors
et al., Topics in Catalysis, 28, 2004, 185).

All of these catalysts exhibit high activity for the selective reduction of NO_x
by hydrocarbons, including long chain alkane and diesel fuel, in the presence of
30 oxygen, but each type of catalyst suffers from some form of limitation in use.
Pt/Al₂O₃ catalysts display lower NO_x conversion and lower selectivity towards
nitrogen; N₂O (conversion >60% in certain conditions) is a basic product.

Additionally, the HC-SCR activity window of Pt/Al₂O₃ catalysts can be limited to low temperatures (150 – 250 °C). Generally speaking, Cu/ZSM-5 catalysts can suffer from thermal deactivation due to copper sintering and dealumination of the zeolite. Ag/Al₂O₃ catalysts are tolerant to hydrothermal ageing, but can suffer from chemical deactivation caused by coking or sulphurisation. We understand that the relatively poor performance of Pt/Al₂O₃ catalysts and the relatively poor activity of Cu/ZSM-5 and Ag/Al₂O₃ HC-SCR catalysts once aged, has so far been insufficient to allow for their widespread commercial implementation (Konig et al., Topics in Catalysis, 28, 2004, 99).

As we disclosed in WO 2005/016496, the coking deactivation of Ag/Al₂O₃ catalysts can be minimised by modifying the catalyst formulation to include components that limit access of the hydrocarbon species responsible for coke deposition on the catalyst. Specifically, we disclosed that by combining known HC-SCR catalysts with a partial oxidation catalyst (POC), it was possible to suppress or avoid low temperature coke formation. In this invention, the POC helps to prevent coking by ensuring that a reduced quantity of, or substantially none of, the heavy hydrocarbon species usually present in exhaust gases (especially diesel exhaust gases) reach an active catalyst's surface. Instead the heavy hydrocarbon species are partially oxidised to smaller, more reactive species upstream of the HC-SCR catalyst.

However, the interaction of SO₂ with the catalyst cannot be satisfactorily altered by changes in the catalyst structure alone. Long term exposure to S-containing fuel can result in poisoning of the catalyst by sulphation.

It is generally known that some catalysts may be desulphated by exposure to high temperature treatment; however, Ag₂SO₄ is a very stable species and requires temperatures in excess of 800 °C to induce its decomposition (see Figure 1). Therefore high temperature treatment is not suitable for use with a Ag/Al₂O₃ catalyst as the temperatures required to decompose Ag₂SO₄ will cause severe sintering of the silver particles resulting in loss of HC-SCR activity. Alternatively, desulphation may be achieved at lower temperatures in stoichiometric, or preferably rich, conditions either by engine calibration or by injecting excess fuel into the exhaust. However,

although exposure of the sulphated $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst to these conditions induces Ag_2SO_4 decomposition, it can also promote the agglomeration of silver particles and deactivation of the catalyst. Furthermore, enriching diesel exhaust is a challenging and complicated procedure due to the presence of a higher amount of oxygen
5 requiring a high concentration of fuel, thus leading to a significant fuel penalty.

A number of previous studies have reported on attempts to regenerate sulphur poisoned $\text{Ag}/\text{Al}_2\text{O}_3$. Hickey et al. (Journal of Catalysis 209, 2002, 271) showed that sulphated $\text{Ag}/\text{Al}_2\text{O}_3$ could not be regenerated by treatment at 450 °C in H_2 , whilst
10 Meunier and Ross (Applied Catalysis B 24, 2000, 23) showed that H_2 reduction could partially regenerate sulphated $\text{Ag}/\text{Al}_2\text{O}_3$ if higher temperatures were used. Similarly, Breen et al. (submitted to Applied Catalysis B) reported that a 2% $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst could be almost fully regenerated when hydrogen was present in the regeneration mix. However these desulphation reactions require the presence of H_2 and were performed
15 under rich conditions, which is difficult to achieve in a diesel exhaust. Furthermore the HC-SCR activity of the desulphated catalyst was measured with a model hydrocarbon, i.e. C_3H_6 which is not representative of the longer hydrocarbon chains found in e.g. diesel fuel.

20 We have now discovered a method for the desulphation of a $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalyst that reduces or avoids excessive fuel penalty and catalyst sintering.

According to a first aspect, the invention provides a method of desulphating a $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalyst in an exhaust system of a lean burn engine, which method
25 comprising contacting the catalyst with a lean exhaust gas stream comprising an elevated quantity of hydrocarbon species relative to normal engine operation at a temperature of from 550 to 700 °C, wherein the hydrocarbon species comprises cracked engine fuel. The inventors did investigate contacting a $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalyst with cracked hydrocarbons at temperatures within the normal temperature
30 range of $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalysts (400 – 550 °C) but found that only partial to ineffective desulphation occurred. Additionally, the inventors investigated contacting a $\text{Ag}/\text{Al}_2\text{O}_3$ HC-SCR catalyst with a range of concentrations of un-cracked

hydrocarbons (i.e. engine fuel) at a range of different temperatures, however they found that this did not result in satisfactory recovery of catalyst activity (see Figure 4).

As described above, the inventors have found that contacting a sulphur-poisoned Ag/Al₂O₃ HC-SCR catalyst with increased levels of cracked hydrocarbons enables the recovery of HC-SCR activity. In one embodiment, the HC-SCR catalyst is contacted with a sufficient quantity of the hydrocarbon species for a sufficient amount of time to result in recovery of at least 50% of original activity in the catalyst for the method to be considered as having resulted in successful desulphation. Whatever the quantity of hydrocarbon contacting the Ag/Al₂O₃ HC-SCR in each case the composition of the exhaust gas for desulphating the Ag/Al₂O₃ catalyst is maintained overall lean.

Prior art exhaust systems comprising: (i) a filter followed by a HC-SCR catalyst, and (ii) a HC-SCR catalyst followed by a filter are known, e.g. from US 2001/005988 and US 2005/103099 respectively. Should the arrangement in either case be such that the filter is actively regenerated by exposing the filter to increased quantities of hydrocarbon, this could result in the HC-SCR catalyst also being contacted by increased levels of hydrocarbon. However, we understand that such prior art arrangements would not fall within the scope of the present invention, for at least the following reasons: (a) the hydrocarbon for regenerating the filter is not necessarily cracked; (b) the temperature of exhaust gas contacting the HC-SCR catalyst is not necessarily within the temperature range 550 to 700 °C; and (c) the quantity of hydrocarbons slipping the filter (in the case of the arrangement disclosed in US 2001/005988) would be up to 2,000 ppm, whilst the amount of hydrocarbon contacting the HC-SCR catalyst upstream the filter would be up to 12,000 ppm.

Therefore, according to one embodiment the method according to the invention comprises contacting the HC-SCR catalyst with a lean exhaust gas stream comprising from 13,000 ppm to 50,000 ppm of hydrocarbon species, optionally from 13,000 ppm to 30,000 ppm. Since injecting increased quantities of hydrocarbon results in increased fuel consumption there is a desire to keep any additional

hydrocarbon demand to a minimum, therefore it is desirable that the quantity of cracked hydrocarbon that contacts the Ag/Al₂O₃ HC-SCR catalyst be minimised.

5 The inventors have found that the hydrocarbon concentration required for satisfactory recovery of catalyst activity is a function of the stoichiometry of the gas mixture. For example, when the inventors carried out tests on a mixture typical of the exhaust gas from a lean burn engine containing 7% CO₂, 4.5% H₂O, 10% O₂, 200 ppm CO and 200 ppm NO_x in N₂, they found that up to 20,000 ppm of hydrocarbon species was required to desulphate a Ag/Al₂O₃ HC-SCR catalyst. Thus although it is
10 desirable to minimise the quantity of additional hydrocarbon nonetheless the quantity of hydrocarbon required to recover a satisfactory level of catalyst activity will vary depending on the stoichiometry of the exhaust gas produced by a particular lean burn engine.

15 The relationship between temperature, hydrocarbon concentration and desulphation of the HC-SCR catalyst is represented in Figure 2.

In one embodiment the in-cylinder injected fuel is cracked in the combustion chamber of the engine to produce shorter chain hydrocarbons. The cracking occurs as
20 the fuel is supplied after the initial combustion has occurred (this is known as post-injection) such that the temperatures and pressures present are sufficient to result in cracking of the fuel but not its complete combustion. In some circumstances the fuel may be injected immediately before the exhaust valves open. Means for achieving post-injection (and thereby the cracking of fuel in the combustion chamber of the
25 engine) include the use of a highly controllable injection system, which is able to provide multiple fuel injections (e.g. up to five) per power stroke. Suitable fuel injection systems include the so-called common rail fuel injection system. Such an injection system includes a control system, such as one able to adjust the fuel injection timing to one or more of the engine cylinders.

30

In an alternative embodiment the fuel is cracked in the exhaust gas stream. The temperature of the exhaust gas may be sufficiently high to break the fuel into the shorter chain hydrocarbons used to desulphate the Ag/Al₂O₃ HC -SCR catalyst.

Alternative means for achieving the cracking of fuel in the exhaust gas stream include the use of an additional injector installed so as to enable the injection of the reductant upstream of a catalyst that promotes cracking of the injected hydrocarbon. Suitable catalysts include POCs; catalysts that promotes the partial oxidation of hydrocarbons in exhaust gas of a lean-burn internal combustion engine to CO, H₂ and partially oxygenated hydrocarbon species (as opposed to complete oxidation to H₂O and CO₂). Patent application WO 2005/016496 discloses POCs suitable for use in the present invention including: (i) a bulk oxide, a bulk composite oxide or a bulk mixed oxide comprising at least one metal selected from the group consisting of manganese (Mn), iron (Fe), cerium (Ce) and praseodymium (Pr); and (ii) at least one of rhodium (Rh) and palladium (Pd) disposed on at least one inorganic oxide support. Such POCs can comprise at least one stabiliser and/or dopant selected from the group consisting of zirconium (Zr), lanthanum (La), aluminium (Al), yttrium (Y), Pr and neodymium (Nd) for group (i), and selected from the group consisting of lanthanum (La), barium (Ba), Ce, tungsten (W), Si and Mn for group (ii).

The hydrocarbon species suited to desulphating the Ag/Al₂O₃ HC -SCR catalyst can include long chain alkanes or alkenes, which may be formed by the cracking of suitable engine fuels such as diesel, gasoline, biodiesel and FT-GTL (Fischer-Tropsch gas to liquids). Therefore, in one embodiment the hydrocarbon species is selected from the group consisting of C₃-C₁₀ alkanes, C₃-C₁₀ alkenes and partially oxidised species with a C₃-C₁₀ length carbon component.

According to a second aspect, this invention provides an exhaust system for a lean burn engine, which system comprising an exhaust system for a lean burn engine, which system comprising a Ag/Al₂O₃ HC -SCR catalyst and means for intermittently contacting the catalyst with a lean exhaust gas stream at a temperature of from 550 to 700 °C, said exhaust gas stream comprising an elevated quantity of hydrocarbon species relative to normal engine operation, thereby to desulphate the catalyst, wherein the hydrocarbon species comprises cracked engine fuel. As in the method according to the invention described above, the elevated quantity of hydrocarbon species found in the lean exhaust gas stream may comprise from 13,000 ppm to 50,000 ppm of hydrocarbon species, optionally from 13,000 ppm to 30,000 ppm.

In one embodiment, the exhaust system may comprise means, when in use, for controlling the supply of the hydrocarbon species. The control means may include a pre-programmed electronic control unit.

5

As in the method according to the invention described above, the engine fuel used to desulphate the Ag/Al₂O₃ HC-SCR catalyst may be cracked in the combustion cylinder of the engine or in the exhaust gas stream, thereby to produce shorter chain hydrocarbons.

10

According to further aspects, the invention provides a lean burn engine including an exhaust system as described above, and a vehicle including such a lean burn engine. Suitable lean burn engines include engines designed to operate using diesel, gasoline, biodiesel and FT-GTL or any combination thereof.

15

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings, in which:

20 Figure 1 is a graph of the temperature programmed decomposition (TPD) of Ag₂SO₄, showing that is a very stable species requiring temperatures in excess of 800 °C to induce its decomposition;

Figure 2 is a representation of how varying the temperature and hydrocarbon species
25 concentration affects the effectiveness of the desulphation process according to the invention;

Figure 3 is a graph comparing the NO_x conversion of fresh, aged and regenerated Ag/Al₂O₃ catalysts, wherein C₃H₆ was used to desulphate the catalyst; and

30

Figure 4 is a graph comparing the NO_x conversion of fresh, aged and regenerated Ag/Al₂O₃ catalysts, wherein US06 diesel fuel was used to desulphate the catalyst.

Example 1**Catalyst Formation**

2 wt% Ag/Al₂O₃ catalysts were prepared by wet impregnation. Silver nitrate was dissolved in the appropriate amount of water according to the pore volume of the alumina support. The nitrate solution was then added to the support with mixing. After drying overnight, the sample was calcined in air at 500 °C for 2 hours.

Example 2**Catalyst Testing**

The initial HC-SCR activity of catalysts prepared according to Example 1 were measured by flowing 2 L/min of a gaseous mixture typical of lean burn engine exhaust gas (NO 500 ppm, US06 (C1 equivalent) 2500 ppm, CO 200 ppm, O₂ 9%, H₂O 4.5%, CO₂ 4.5%, with or without 4000 ppm H₂, balance N₂) over 0.4 g catalyst to give the "Fresh" results in Figures 3 and 4. NO_x conversions were typically measured after 15 mins at constant temperature starting from 200 °C and increasing the temperature in 50 °C intervals to 500 °C. We refer to this as steady-state NO_x conversion.

The catalysts were sulphated at a temperature of 350 °C with 2 L/min flow rate of NO 500 ppm, SO₂ 200 ppm, H₂O 4.5%, balance air for 2 hours. This resulted in an exposure of 70 mg sulphur per gram of catalyst. The HC-SCR activity of the sulphur aged catalysts were measured to give the "1st S Aged" results in Figures 3 and 4.

The catalyst was desulphated at a temperature of from 550 to 700 °C with 2-3 L/min flow rate of a gas mixture containing 20,000 ppm C₃H₆ (C1 equivalent) in addition to the lean burn engine exhaust gas mixture. (Since the average chemical formula for common diesel fuel is C₁₂H₂₆, ranging from approximately C₁₀H₂₂ to C₁₅H₃₂, C₃H₆ was used to mimic cracked diesel fuel.) The HC-SCR activity of the catalyst regenerated using C₃H₆ was measured to give the "1st S Aged, Regenerated" results in Figure 3.

Repeated sulphation and desulphation cycles were carried out using C_3H_6 to regenerate the catalyst, the HC-SCR activity of which was then measured using US06 (as described above). The HC-SCR activity of the repeatedly aged and regenerated catalyst is shown in Figure 3 as the “2nd S Aged”, “2nd S Aged, Regenerated”, “3rd S Aged” and “3rd S Aged, Regenerated” results.

Desulphation experiments were also carried out using US06 diesel fuel in place of C_3H_6 . The results of a single desulphation reaction using US06 may be seen in Figure 4 as “1st S Aged, Regenerated”.

Figures 3 and 4 show that a Ag/Al_2O_3 catalyst may be successfully desulphated to regain catalytic NO_x conversion activity, even after several sulphation / desulphation cycles, using a short chain hydrocarbon (such as that which would be produced by cracking diesel fuel) but not using diesel fuel itself.

CLAIMS:

1. A method of desulphating a $\text{Ag/Al}_2\text{O}_3$ hydrocarbon selective catalytic reduction (HC-SCR) catalyst in an exhaust system of a lean burn engine, which
5 method comprising contacting the catalyst with a lean exhaust gas stream comprising an elevated quantity of hydrocarbon species relative to normal engine operation at a temperature of from 550 to 700 °C, wherein the hydrocarbon species comprises cracked engine fuel.
- 10 2. A method according to claim 1, wherein the lean exhaust gas stream comprises from 13,000 ppm to 50,000 ppm of hydrocarbon species, optionally from 13,000 ppm to 30,000 ppm.
3. A method according to claim 1 or 2, wherein the fuel is cracked in the
15 combustion cylinder of the engine.
4. A method according to claim 1 or 2, wherein the fuel is cracked in the exhaust gas stream.
- 20 5. A method according to any preceding claim, wherein the hydrocarbon species is selected from the group consisting of $\text{C}_4\text{-C}_{10}$ alkanes, $\text{C}_4\text{-C}_{10}$ alkenes and partially oxidised species with a $\text{C}_3\text{-C}_{10}$ length carbon component.
- 25 6. An exhaust system for a lean burn engine, which system comprising a $\text{Ag/Al}_2\text{O}_3$ HC-SCR catalyst and means for intermittently contacting the catalyst with a lean exhaust gas stream at a temperature of from 550 to 700 °C, said exhaust gas stream comprising an elevated quantity of hydrocarbon species relative to normal engine operation, thereby to desulphate the catalyst, wherein the hydrocarbon species comprises cracked engine fuel.
- 30 7. An exhaust system according to claim 6, wherein the lean exhaust gas stream comprises from 13,000 ppm to 50,000 ppm of hydrocarbon species, optionally from 13,000 ppm to 30,000 ppm.

8. An exhaust system according to claim 6 or 7, comprising means, when in use, for controlling the supply of the hydrocarbon species.

5 9. An exhaust system according to claim 8, wherein the control means includes a pre-programmed electronic control unit.

10. An exhaust system according to any of claims 6 to 9, comprising means for cracking the engine fuel in the combustion cylinder of the engine.

10

11. An exhaust system according to claim 10, wherein the cracking means comprises a highly controllable injection system.

12. An exhaust system according to any of claims 6 to 9, comprising means for
15 cracking the engine fuel in the exhaust gas stream.

13. An exhaust system according to claim 12, wherein the cracking means comprises an additional injector located such that it injects directly into the exhaust gas stream upstream of at least one partial oxidation catalyst (POC).

20

14. An exhaust system according to claim 13, wherein the at least one POC is selected from the group consisting of: (i) a bulk oxide, a bulk composite oxide or a bulk mixed oxide comprising at least one metal selected from the group consisting of manganese (Mn), iron (Fe), cerium (Ce) and praseodymium (Pr); and (ii) at least one
25 of rhodium (Rh) and palladium (Pd) disposed on at least one inorganic oxide support.

15. A lean burn engine including an exhaust system according to any of claims 6 to 14.

30 16. A vehicle including a lean burn engine according to claim 15.

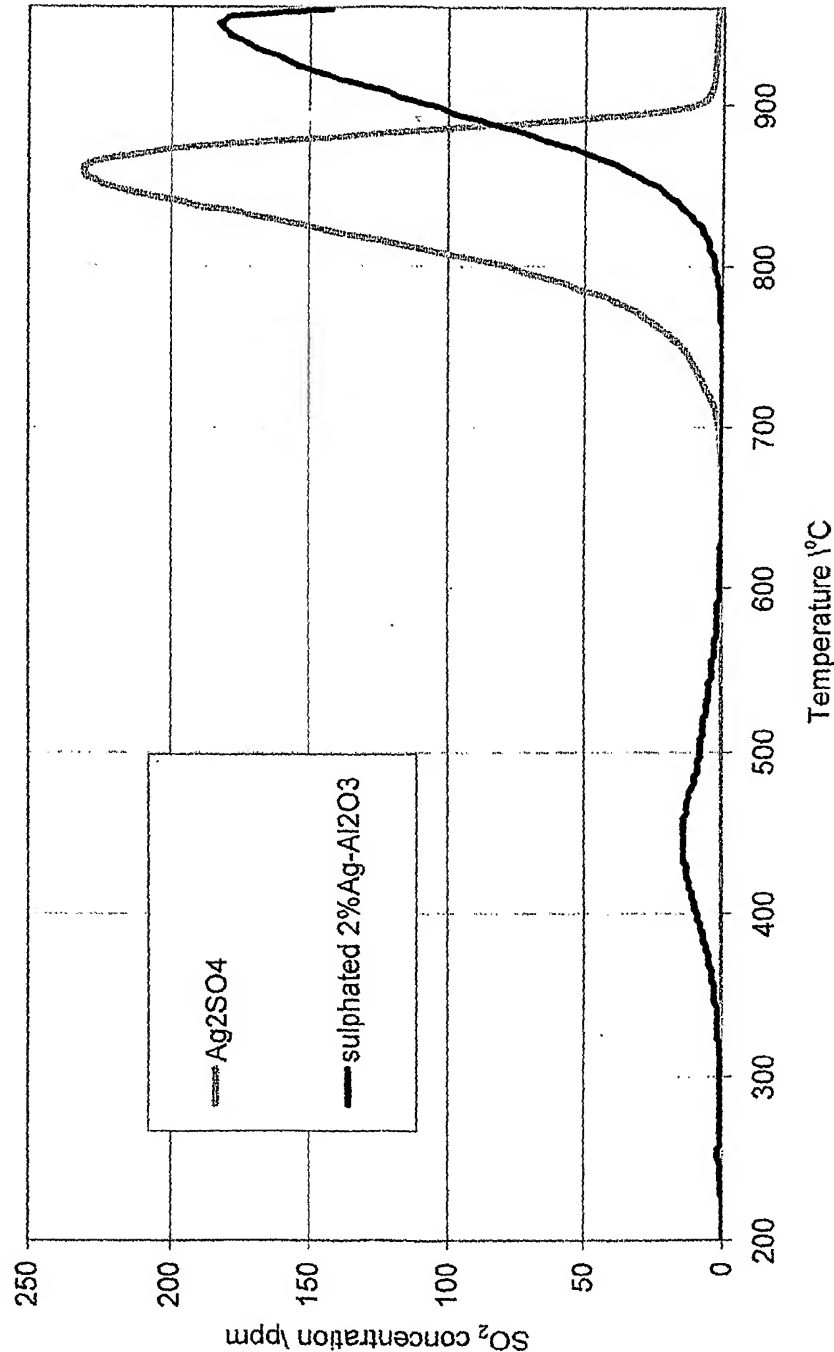


Figure 1

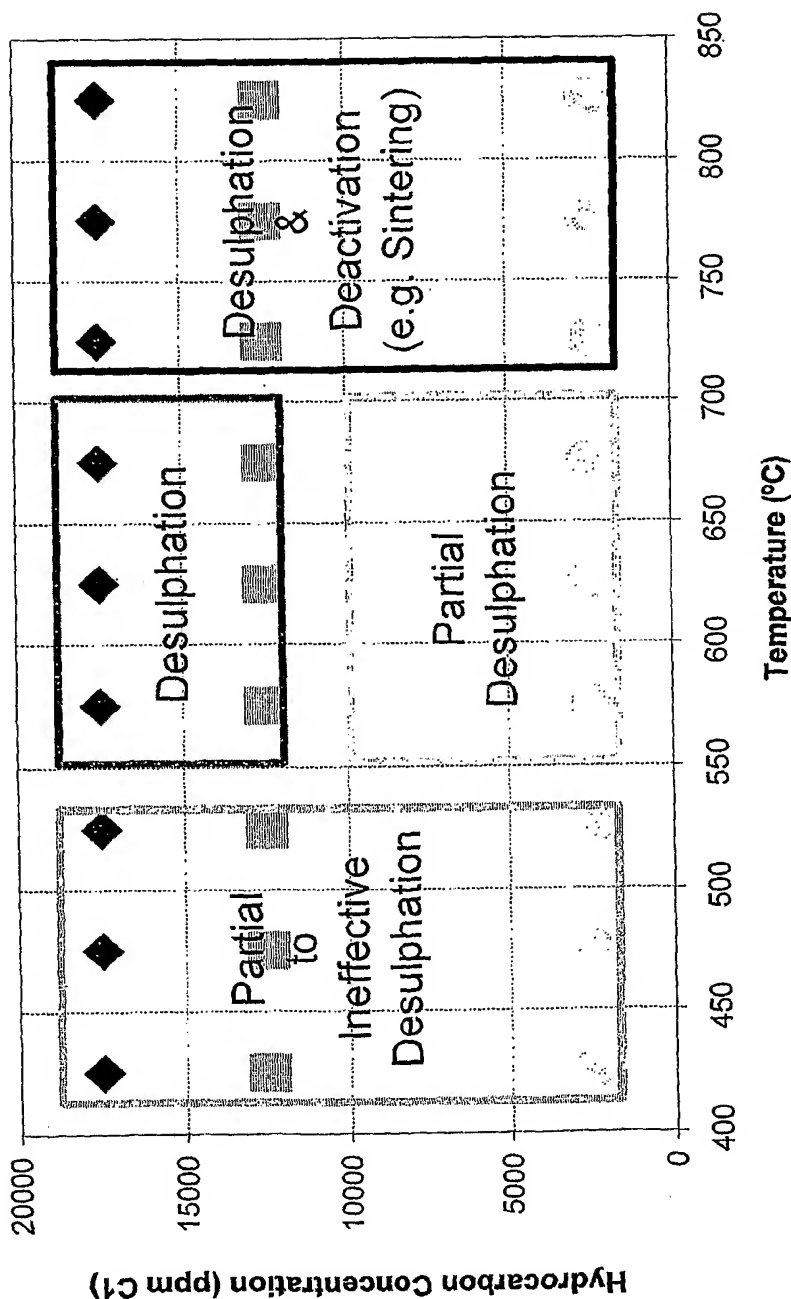


Figure 2

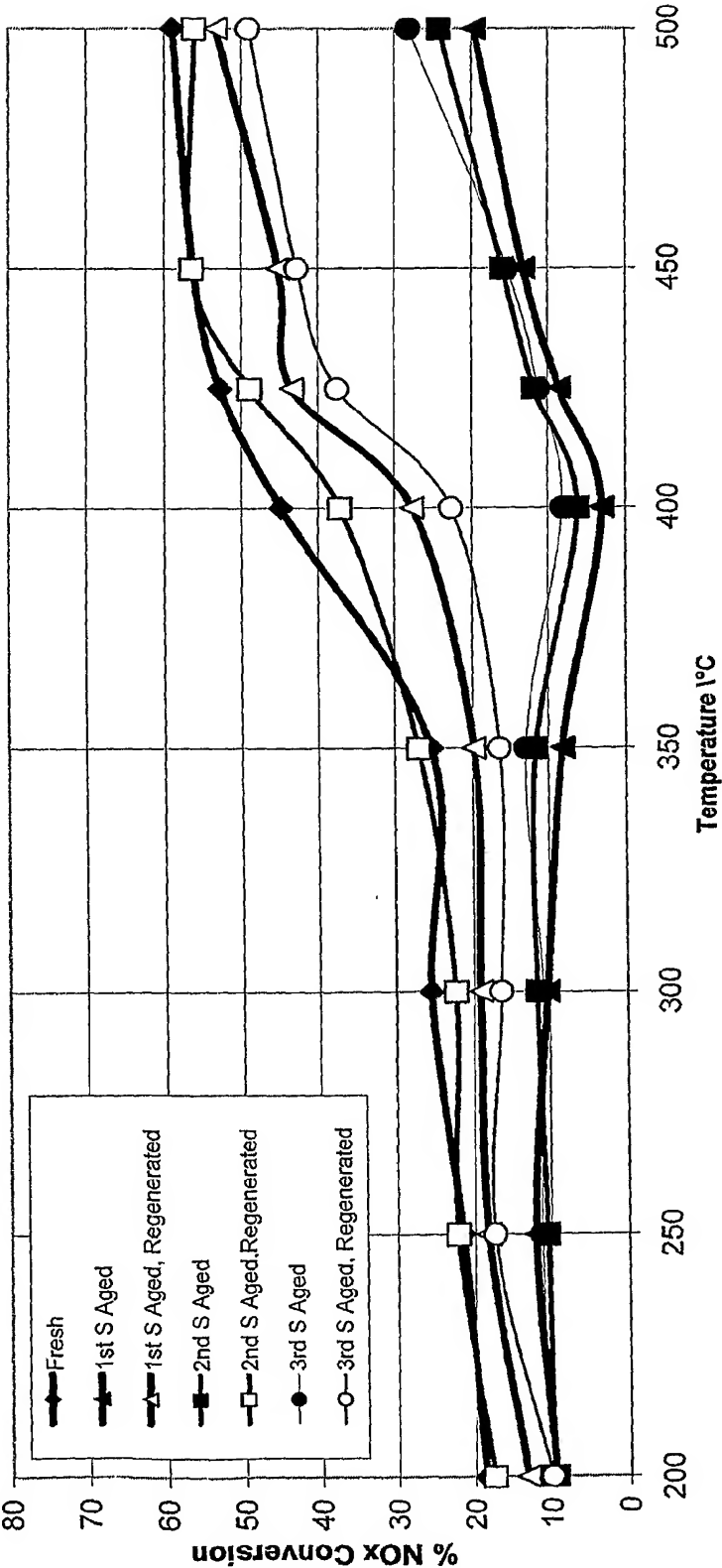


Figure 3

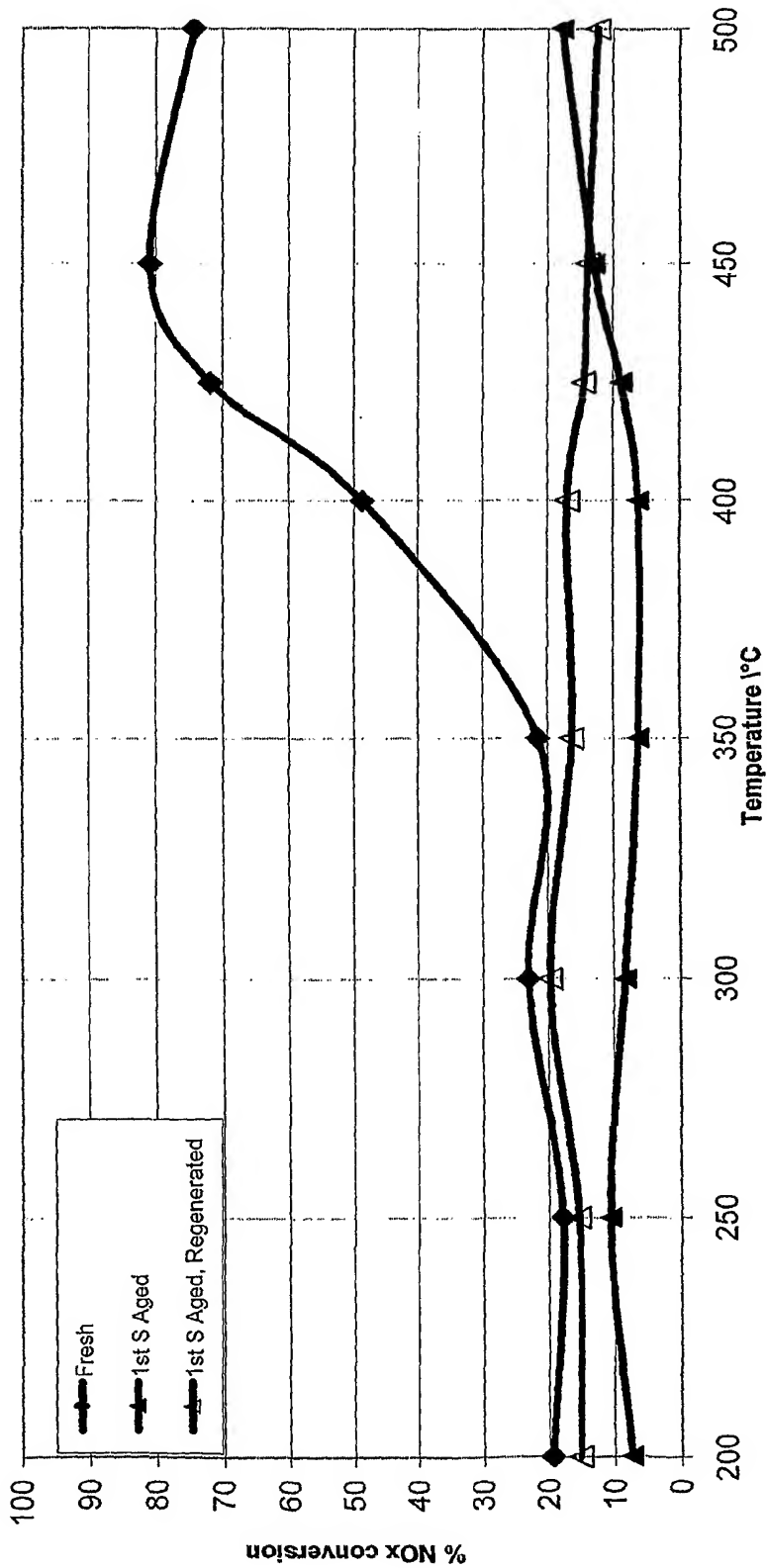


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/002595

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J23/50 F02D41/02 B01D53/94 F01N3/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01J F02D B01D F01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 1, line 47 - line 51 column 4, line 19 - line 24 column 4, line 47 - column 54 column 5, line 32 - line 45 column 6, line 54 - line 67 column 7, line 58 - line 63 column 11, line 55 - column 12, line 41 figures 1-6	1-16
Y	----- EP 1 264 978 A (NISSAN MOTOR [JP]) 11 December 2002 (2002-12-11) paragraphs [0003], [0004], [0009] - [0011], [0037], [0044], [0049], [0070]; figure 1 claims 1,10,11 ----- -/--	1-16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 27 October 2006		Date of mailing of the international search report 06/11/2006
Name and mailing address of the ISA/ European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Gosselin, Daniel

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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